

Adsorption Dynamics of Binary System (Varying Pressure Steps)

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Abstract

The separation of a binary system by a cyclic pressure swing technique using Molecular Sieves usually consists of four general steps. They are pressurization, adsorption, depressurization and purge steps. This work discusses a method of predicting the varying pressure steps theoretically when pure component isotherms and the knowledge of relative adsorptivity are available. The comparison of computer results using method of characteristics with the experimental data is presented.

The separation of a gas or liquid mixtures by adsorption technique has traditionally been carried out under constant pressure. In other words, the regeneration of the saturated bed was normally achieved by thermal means by simply raising the temperature of the fixed bed. When the bed is relatively large, however, this step takes considerable amount of time which in turn causes an increase in the required adsorbent. To alleviate this difficulty, a method of regenerating the saturated bed by lowering the system pressure has been recently developed. Since this technique does not involve the slow heat transfer step, it is rapid and efficient. In actuality, a typical cyclic operation using 2 or 3 fixed beds in parallel would involve:

1. Pressurization of the fixed bed with a feed mixture.
2. Perform adsorption operation at this high pressure until the bed is saturated.
3. Depressurize (below down) the bed to a low

pressure, usually atmospheric, to get rid of some adsorbed adsorbate.

4. Perform a purge operation at this low pressure to expel the system.

The purge operation described in step 4 has been discussed earlier.⁽¹⁾ Present work discusses the operations involved in steps 1 and 3. As before,⁽¹⁾ the assumptions of isothermal operation and an equilibrium between the gas and solid phases were assumed in making the analyses.

Governing Equations

The material balance equation applying for a small increment " dl " of the fixed bed was shown to be as follows.⁽¹⁾

$$-\frac{\partial(Gy)}{\partial t} = \epsilon \frac{\partial(y\rho_g)}{\partial t} + \rho \frac{\partial W_N}{\partial t}; \text{ component balance} \quad (1)$$

$$-\frac{\partial G}{\partial t} = \epsilon \frac{\partial \rho_g}{\partial t} + \rho \frac{\partial W_T}{\partial t}; \text{ overall balance} \quad (2)$$

In the case of varying pressure, however, need somehow to introduce " p " as an independent variable. To accomplish this, we have decided to neglect existence of a small pressure gradient in the longitudinal direction of the bed. The bed pressure at any

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given instant and at any point in the bed can simply be related to time, *i. e.*

$$t = \phi(p) \quad (3)$$

We can also define a new quantity of flow rate Q as follows.

$$Q = G \left(\frac{ft^3 \text{ of gas N. T. P.}}{ft^2 \text{ of area. hr}} \right) \frac{dt}{dp} \left(\frac{hr}{atm.} \right) \\ = G \frac{d\phi}{dp} \left(\frac{ft^3}{ft^2 atm.} \right) \quad (4)$$

As a next step, with slight algebraic manipulation, the governing equation then can be rearranged as follows.

$$-\frac{\partial(Qy)}{\partial l} = \epsilon \frac{\partial(\rho_g y)}{\partial p} + \rho \frac{\partial W_N}{\partial p} \quad (5)$$

$$-\frac{\partial Q}{\partial l} = \epsilon \frac{\partial \rho_g}{\partial p} + \rho \frac{\partial W_T}{\partial p} \quad (6)$$

These equations have to be solved with proper initial and boundary conditions. More specifically, for depressurization we can state:

$$1. \text{ At } p = p_i, \quad y = f_1(l) \text{ or } y = y_i \quad (7)$$

$$2. \text{ At } l = 0, \quad Q = 0 \quad (8)$$

While, for pressurization, we can say

$$1. \text{ At } p = p_i, \quad y = f_2(l) \text{ or } y = y_i \quad (9)$$

$$2. \text{ At } l = 0, \quad Q = 0 \quad (10)$$

$$3. \text{ At } l = L, \quad y = f_3(p) \text{ or } y = y_L \quad (11)$$

Coadsorption Isotherm

The governing equations (5) and (6) are difficult to solve as they stand but can be made amenable to mathematical analyses by introducing the coadsorption isotherm expression.

These were shown to be ^{(1) (2)}.

$$W_N = \frac{\bar{W}_N}{1 + \frac{1-y}{\alpha y} \left(\frac{\bar{W}_N}{\bar{W}_0} \right)} \quad (12)$$

$$W_T = W_N \left(1 + \frac{1-y}{\alpha y} \right) \quad (13)$$

Furthermore, for a fairly large range of pressures, the pure component isotherms, \bar{W}_N and \bar{W}_O as well as the relative adsorptivity can be expressed as

$$\bar{W}_N = C_1 p^{C_2} \quad (14)$$

$$\bar{W}_O = C_3 p^{C_4} \quad (15)$$

$$\alpha = C_5 p^{C_6} \quad (16)$$

Substitution of the last three equations into (12) and (13) now gives

$$W_N = \frac{a p^h}{1 + \left(\frac{1-y}{y} \right) b p^i} = f_4(p, y) \quad (17)$$

$$W_T = \frac{a p^h + \left(\frac{1-y}{y} \right) c p^k}{1 + \left(\frac{1-y}{y} \right) b p^i} = f_5(p, y) \quad (18)$$

where $a = C_1$

$$b = \frac{C_1}{C_3 C_5} \quad (19)$$

$$c = \frac{C_1}{C_5}$$

$$h = C_2$$

$$i = C_2 - C_4 - C_6 \quad (20)$$

$$k = C_2 - C_4$$

Equations (17) and (18) in essence express coadsorption isotherms as functions of a pressure and a gas phase concentration. We therefore can proceed to differentiate the expression as shown below.

$$\frac{\partial W_N}{\partial p} = \frac{\partial f_1}{\partial p} + \frac{\partial f_1}{\partial y} \frac{\partial y}{\partial p} = \lambda_n + \phi_n \frac{\partial y}{\partial p} \quad (21)$$

$$\frac{\partial W_T}{\partial p} = \frac{\partial f_2}{\partial p} + \frac{\partial f_2}{\partial y} \frac{\partial y}{\partial p} = \lambda_T + \phi_T \frac{\partial y}{\partial p} \quad (22)$$

The λ 's and ϕ 's can be shown to be:

$$\lambda_n = \frac{\partial f_1}{\partial p} = \frac{a[h + (s-1)(h-i)]}{p^{1-h} s^2} \quad (23)$$

$$\lambda_T = \frac{\partial f_2}{\partial p} = \lambda_n + \frac{c Y[k + (s-1)(k-i)]}{p^{1-k} s^2} \quad (24)$$

$$\phi_n = \frac{\partial f_1}{\partial y} = \frac{ab p^{h+i} (1+Y)^2}{s^2} \quad (25)$$

$$\phi_T = \frac{\partial f_2}{\partial y} = \phi_n - \frac{c p^k s^2 (1+Y)^2}{s^2} \quad (26)$$

$$\text{where } Y = \frac{1-y}{y} \quad (27)$$

$$s = 1 + b Y p^i \quad (28)$$

The gas density in the void volume is easily related to pressure by assuming it to behave ideally.

$$\rho_g = \beta p = \frac{294.4}{T(^{\circ}K)} p \quad (29)$$

Substitution of equations (23), (24), (25), (26) and (29) into (5) and (6) then gives

$$-\frac{\partial(Qy)}{\partial l} = A + B \frac{\partial y}{\partial p} \quad (30)$$

$$-\frac{\partial Q}{\partial l} = C + D \frac{\partial y}{\partial p} \quad (31)$$

where

$$A = \epsilon \beta y + \rho \lambda_n$$

$$B = \epsilon \beta p + \rho \phi_n$$

$$C = \epsilon \beta + \rho \lambda_T \quad (32)$$

$$D = \rho \phi_T$$

It must be noted that all the coefficients A , B , C and D are functions of p and y only. In this manner, therefore, we have reduced the original equations (5) and (6) to a tractable form.

Numerical Solution of Equations by Method of Characteristics

The set of partial differential equations to be solved are totally hyperbolic. The method of characteristics therefore is suitable in carrying out the numerical solution along the line of adsorption wave propagation. ⁽³⁾

To find these characteristic directions it is necessary first of all to slightly transform equations (30) and (31). It can be seen that as these equations stand, each involves different directional derivatives of each of the two dependent variables. Thus, (31) contains a derivative of Q in the direction, but a derivative of y in the p direction; and (32) also contains a derivative of Q in the l direction, but a derivative of y in still another direction.

If, however, (30) is multiplied by the coefficient D , and (31) by the coefficient B , and the results subtracted, the net result is

$$B \frac{\partial Q}{\partial l} - D \frac{\partial(Qy)}{\partial l} = AD - BC \quad (33)$$

Expansion of the derivative of the product, Qy , and division by $(B-Dy)$ yields

$$\frac{\partial Q}{\partial l} - \frac{QD}{B-Dy} \frac{\partial y}{\partial l} = \frac{AD-BC}{B-Dy} \quad (34)$$

Thus, a new differential equation is obtained, in which both Q and y are differentiated in the l direction, or along a curve in the l, p plane with a slope

$$\frac{dp}{dl} = 0 \quad (35)$$

Similarly, if the right-hand side of (21) is substituted for $\frac{\partial Q}{\partial l}$ in (30) the result is:

$$\frac{Q}{B-Dy} \frac{\partial y}{\partial l} + \frac{\partial y}{\partial p} = -\frac{A-Cy}{B-Dy}$$

According to calculus, this can also be written

$$\frac{dy}{dp} = -\frac{A-Cy}{B-Dy} \quad (36)$$

along a path in the l, p plane whose derivative is

$$\frac{dl}{dp} = \frac{Q}{B-Dy} \quad (37)$$

In carrying out the numerical computation, therefore, equation (34) is solved along (35) while (36) is used in the direction specified by (37).

Depressurization

The $p-l$ plane for depressurization is shown in Figure 1. The first characteristic line is simply the integration of (35) which is

$$p = \text{constant} \quad (38)$$

Equations (34), (36) and (37) are then solved simultaneously to get the other family of characteristics. In Figure 1, the closed end of the bed is at $l=0$, and the open end is at $l=L$. Upon depressurization, gas flows outward, from left to right.

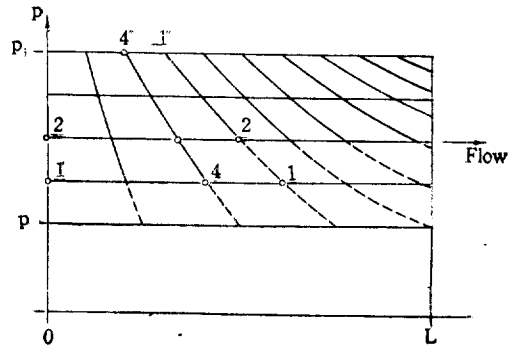


Fig. 1. Depressurization

Suppose, now, we wish to compute the values of l, Q and y at 1 from the knowledges at 2 and 4. First, a finite difference version of equation (34) is applied to the segment 2-1. The computation is done iteratively, starting with coefficients in (34), (36), and (37) evaluated at points 4 and 2. As tentative values are obtained for l, y, Q at point 1, new coefficients are computed for the finite-difference equations, based on average values of p, y , and Q along the segments 4-1 and 2-1. Usually only a few iterative cycles are needed for effective convergence.

To start along each new constant pressure line, however, it is necessary to compute the first pivotal point on that line, at the intersection of the p -axis, by a slightly different technique than has heretofore been described. Thus, to start computations along the pressure characteristic passing through points 1

and 1' of the figure it would be necessary initially to use known values of p , l , y , and Q at point 2' to compute similar values at point 1'. Actually, since point 1' lies on a boundary (the closed end of the bed), some values for point 1' are known in advance; specifically, values of p , l , and Q . The value of y for point 1' is obtained by applying the finite-difference version of equation (36) to the boundary segment 1'-2'. Again, the computation on segment 1'-2' is iterative.

A slight variation of this procedure is of course required for the zeroth pressure step, *i.e.*, for evaluating pivotal points along the horizontal characteristic associated with the initial pressure, p_i . Some, but not all, of the values are given as initial conditions for the problem: values of p , l , and y are given at all pivots, but values of Q must be computed. Because no inertial terms have been provided in the mathematical, it is not possible to specify Q independently at initial time. Rather, Q is, initially, whatever is required by the model to be consistent with initial values of y . Thus, initially, equation (34) must be applied all along the characteristic p_i , to get the consistent relation of Q vs. l .

Pressurization

Much of pressurization proceed in an exactly analogous fashion, except for using a pressure **increment**, characterized by a positive value of Δp , rather than a **decrement** as was employed for **depressurization**. With this change in sign of Δp , all the formulas involved automatically adapt themselves to the pressurization process. The initial concentration profile of y vs l must now, however, be specified at

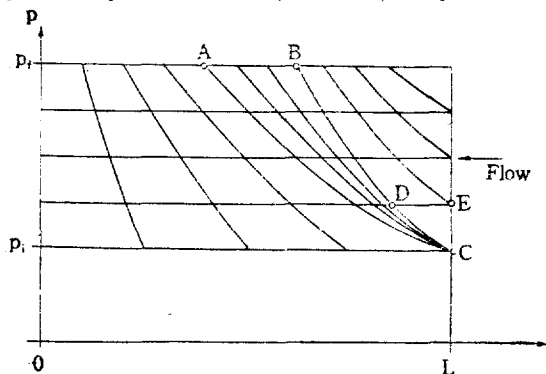


Fig. 2. Pressurization

the lowest pressure level, which is the initial bed pressure. And now the stepwise computation develops the characteristic curves of the second category in a direction proceeding upwardly and to the left.

Again, the closed end of the bed is at $l=0$, and the open end at $l=L$. But now the flow direction is reversed, with gas flowing from right to left.

Note that insofar as propagation of the solution of the pressurization case is upward and to the left, the fifth characteristic curve, AC , of the sketch forms a natural demarcation. The region to the left of AC in the l, p plane represents states attained by gas that was in the bed initially, and the region to the right represents states attained by gas which has entered the bed during pressurization.

The region to the right of AC consists of two subregions separated by characteristic BC , and note also that the point C is distinguished by having a multiplicity of characteristics pass through it. (Again it should be pointed out that only a few of the infinitely many curves belonging to the respective families of characteristics have been shown on the sketch; actually, infinitely many characteristics through C and occupy the region ABC). The reason for such abnormal behavior lies in the condition assumed for the entering gas mixtures. Only would the concentration of the entering gas be in equilibrium with the bed entrance in its initial state. In most cases of practical importance, the entering gas will have a lower gas concentration than that in equilibrium with the bed entrance. Accordingly, a discontinuity arises, and the fan of characteristics occupying area ABC represents the propagation of this initial discontinuity.

To originate this fan of curves, one can apply a degenerate form of equation (34) at the singular point C :

$$\frac{dQ}{dy} = \frac{QD}{B-Dy} \quad (38)$$

Using the finite-difference equivalent of (38) one generates as many pairs of y, Q values as desired over the interval $y_c' < y < y_c$, where y_c is the initial concentration of gas in equilibrium with the bed at the point of entrance, and y_c' is the initial concentration of the feed.

This peculiar treatment of the fan of characteristics through point C is required only at the initial pressure level. At the next higher pressure level (passing through D and E), the lattice points defined by the intersection of the pressure characteristic with the fan of characteristics emanating from point C succumb nicely to the iterative routine for general interior points. One slight abnormality is encountered, however, with respect to point E . This is a pivotal point on the boundary representing the open end. That particular boundary is not a characteristic curve. Generally, entering values of y will be specified at pivotal points along it, but despite the fact that it is non-characteristic, arbitrary values of Q cannot be specified along it without producing shocks. To find the appropriate value of Q at point E , the finite difference equivalent of equation(34) is applied to the segment DE , utilizing known functional values at point D , (which have been obtained by starting at the p axis and stepping from left to right along the characteristic through D and E), and using the prescribed value of y at point E . The solution thus obtained for point E originates a new characteristic

of the second class, rising upward from E . Each remaining pivotal point on the entrance boundary is treated similarly. Thus, each increase in pressure level originates one more characteristic for the computing lattice.

Results

The computer calculation was carried out with Burrough Corporation's Datatron 205. The experimental data were obtained from the 6 inches diameter, 13 feet high adsorber at the Linde laboratory using rapid sampling system. The system studied were those of N_2 - O_2 -Molecular Sieves 5A. The required isotherms and relative adsorptivities were measured by R. J. Neddenriep.

The results of computer calculations are shown in Figure 3 along with the experimental points. One can also compute the effluent volume and concentration. In this particular instance, between 2.7 and 2.3 atm. was considered to be O_2 rich product while those between 1.49 and 1.0 atm. was thought of as blow down gas to be discarded. The comparison are shown below.

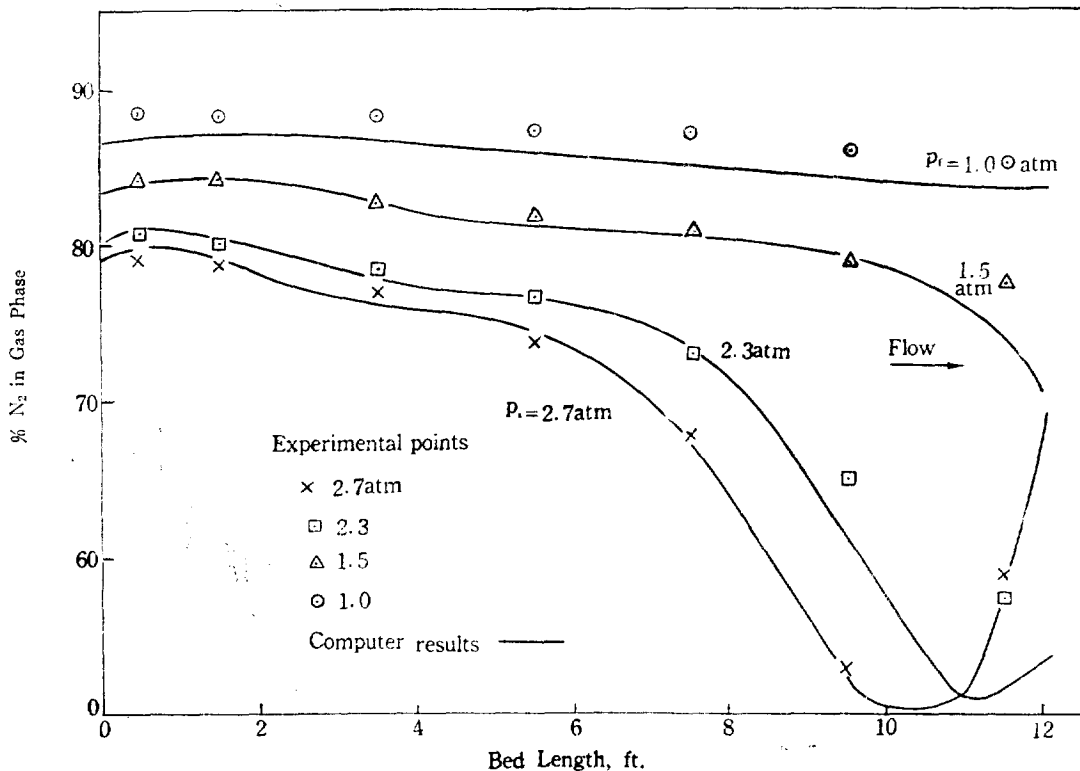
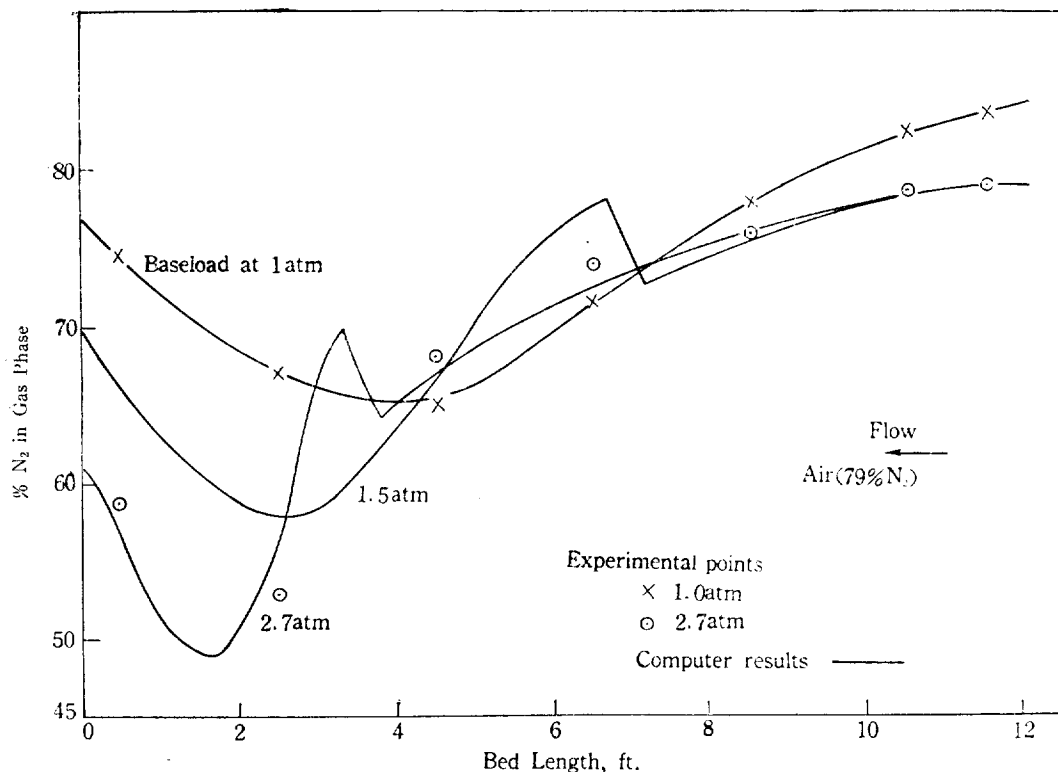


Figure 3. Depressurization of nonuniformly loaded bed Molecular Sieves 5A- N_2 - O_2 system



Figur 4. Pressurization of nouniformly loaded bed Molecular Sieves 5A-N₂-O₂ system

	Pressure:		Computer results	Pilot plant
	From	To		
Product vol.	2.7atm	2.3atm	294ft ³	3.03ft ³
Product conc.	2.7atm	2.3atm	42.05% O ₂	41%
Blowdown vol	1.49	1.0	4.916	4.65

The results in the case of pressurization is shown in Figure 4. The shock wave bump pattern predicted by computer particularly should benoted. The experimantal vertication of this pattern was difficult due to the large distances between the sample probes. The comparison of air volume required to do the pressurization is shown below.

	Computer results	Pilot plant
ft ³ of air required to pressuize the 110 pound bed from 1.0 atm. to 2.7 atm.	16.2	14.3

Nomenclature

G =Total flow rate gas at constant pressure
(ft³ N. T. P./ft²hr)

l =Lengh of the fixed bed (ft)

t =Elapsed time (hr)

y =Mol fraction of N₂ in gas phase
(dimensionless)

ϵ =Void fraction (0.52 for CaA, CaX Molecular Sieves)

ρ_g =Density of a gas mixture (ft³ N. T. P./ft³ of bed)

ρ =Bulk density of the bed (lb of adsorbent/ft³ of bed)

W_N =Coadsorption loading of N₂ (ft³ N. T. P./lb of adsorbent)

W_T =Total loading of O₂-N₂ mixture (ft³ N. T. P./lb of adsorbent)

p =System pressure (atm. abs.)

Q =Flow rate in varying pressure system, defined by (ft³ N. T. P./ft² atm.)

ϕ =Defined by (3)
 α =Relative adsorptivity (dimensionless)
 C_1, C_2, C_3, C_4 =Constants associated with Freundlich isotherms, defined by (14) and (15)
 C_5, C_6 =Constants needed to relate α and p as defined by (16)
 a, b, c, h, i, k =Constants relating coadsorption loadings as defined in equations (19) and (20).
 λ_a, λ_T =Coefficients defined by (23) and (24)
 ϕ_n, ϕ_T =Coefficients defined by (25) and (26)
 Y =Defined by (27)
 s =Defined by (28)
 $p=294.4/T(^{\circ}\text{K})$ as defined by (29)
 T =System temperature ($^{\circ}\text{K}$)
 A =Defined by (32); or cross sectional area of flow (ft^2)

B, C, D =Defined by (32)
 N =Subscript indicating N_2
 O =Subscript indicating O_2
 i =Subscript indicating final condition
 $--$ =Symbol used to indicate pure component quantity. W_N for example is the loadin of pure N_2
 L =Total length of the fixed bed (ft)

References

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